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(54)【発明の名称】 固形状活性炭及びそれを用いた電気二重層コンデンサ

(57)【要約】

【課題】高電流放電時の静電容量に対する低電流放電時の静電容量の容量比が大きく、かついずれの放電時にも実用的な静電容量を有し、良好な成形性と機械的強度の大きい耐久性に優れた各種用途に適用可能な固形状活性炭と、それを分極性電極として用いた実用的な電気二重層コンデンサを提供する。

【解決手段】活性炭粉末及び／又は活性炭繊維等から成る炭素質を主体とする分極性電極材料と、それを100重量部とした時、0.5～10重量部の割合から成るカーボンブラックを含有してなるもので、300mA/cm²の高電流と30mA/cm²の低電流の定電流放電法で静電容量を測定した場合、前記高電流放電時の静電容量に対する低電流放電時の静電容量の容量比が40.0%以上である固形状活性炭。

【特許請求の範囲】

【請求項1】炭素質を主体とする分極性電極材料100重量部に対して0.5～10重量部のカーボンブラックを含有して成り、300mA/cm²の高電流と30mA/cm²の低電流の定電流放電法で静電容量を測定した時、前記高電流放電時の静電容量に対する低電流放電時の静電容量の容量比が40.0%以上であることを特徴とする固形状活性炭。

【請求項2】請求項1に記載の固形状活性炭を分極性電極としたことを特徴とする電気二重層コンデンサ。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、電気二重層コンデンサやリチウムイオン電池をはじめとする小型大容量のコンデンサや、バックアップ電源、車両用電源、補助電源等の各種電池に用いられる電極材料、あるいはガス吸着剤や上水用、食品精製用、排水浄化用の濾材等に用いられる多孔質の活性炭焼結体として一般に広く適用し得る固形状活性炭及びそれを用いた電気二重層コンデンサに関するもので、とりわけ静電容量が大きく、エネルギー密度が大きな電力用蓄電システムを実現可能とする固形状活性炭及びそれを分極性電極として用いた電気二重層コンデンサに関するものである。

【0002】

【従来の技術】近年、活性炭はその特性に着目した各種応用分野への適用が検討されているが、特に小型大容量のコンデンサや、各種電池の電極材料用の多孔質炭素材料として前記活性炭が注目され、種々検討が成されている。

【0003】なかでも前記活性炭をはじめとする炭素質を主体とする分極性電極は、該分極性電極間に電解質を介在させ、両者の界面で形成される電気二重層を利用した、従来のコンデンサに比較して単位体積当たり数千倍にも及ぶ静電容量を有する電気二重層コンデンサ用として多用されている。

【0004】かかる電気二重層コンデンサは、コンデンサと電池の両方の機能を有することから、小型のメモリアップバックアップ電源や大容量のモーター等の補助電源に適用される等、エレクトロニクス分野の発展と共に急速にその需要が伸びている。

【0005】当初、前記電極材料としては、一般に広く適用される多孔質の固形状活性炭が用いられており、そのような固形状活性炭としては、例えば、活性炭等の炭素質と、四フッ化エチレン樹脂又は含フッ素重合体等の有機樹脂を混練してロール成形法や圧縮成形法等、公知の成形手段でシート状に成形したもの等が用いられていた。

【0006】しかしながら、前述のようなコンデンサや電池の電極材料としては、とりわけ高い静電容量と低い内部抵抗という性能を満足し、かつ昨今の電子部品の小

型化の要求を満足するために、所定容量に対する体積の極小化、及び電解液の含浸性を考慮した多孔体構造で亀裂や破損等を起こし難い等と共に、一般的な特性としても更に耐久性と機械的特性に優れたものであること等が要求されるようになってきた。

【0007】そこで、前記諸要求を満足するために、活性炭微粒子、又はカーボン微粒子とカーボン繊維、又は活性炭粉末とメソフェーズ系カーボン等を混合して加圧焼結したり、あるいは活性炭粉末と粉末状フェノール樹脂を有機溶剤に溶解させた混合物を基板上に成膜し、加熱硬化後、非酸化性雰囲気中で熱処理した後、賦活処理する等、各種製造方法による固形状活性炭が提案されていた。

【0008】しかしながら、かかる固形状活性炭は耐久性や機械的強度を損なわない範囲で比表面積を大きくした多孔質の活性炭と前記有機樹脂との混合物から製造されており、該活性炭の充填量は全細孔容積との関係から一定範囲に制約され、しかも成形性の良好な前記有機樹脂は、活性炭の微細孔を塞いでしまう可能性が高く、前記活性炭の充填量とも相まって比表面積が更に減少し、いずれも前記静電容量に対する体積の極小化という点からは満足するものではなかった。

【0009】一方、前記活性炭の微細孔を塞ぐことのない高粘度の有機樹脂を用いた場合には、成形性が悪いことから炭化熱処理後の機械的強度も極めて低いという欠点があった。

【0010】かかる問題を解消するために、活性炭基材に炭素化合物から成るアルカン類やアルケン類、アルコール等の有機溶剤を含浸させてから、更に有機樹脂から成るバインダーを添加混合して活性炭電極を製造する方法等が提案されている（特開平8-138979号公報参照）。

【0011】

【発明が解決しようとする課題】しかしながら、前記活性炭電極は、その静電容量を定電流放電法で測定した場合、活性炭と各種有機樹脂との割合から予測される静電容量より低かったり、あるいは30mA/cm²程度の低電流で放電すると20F/cc程度の静電容量が得られたとしても、逆に300mA/cm²程度の高電流で放電した場合には静電容量が5F/cc程度と極めて低く、高電流放電時の静電容量に対する低電流放電時の静電容量の容量比が20%程度と低くなるものがあり、例えば、電気二重層コンデンサの分極性電極用としては適用できるものの、モーター等の補助電源等、高電流放電時の静電容量を必要とする用途には適用できず、用途が限定され多目的の固形状活性炭としては採用できないという課題があった。

【0012】また、前記活性炭電極の製造方法では、アルカン類やアルケン類等の有機溶剤では可塑化しないため、造粒体が硬く取り扱いの容易な成形体を得られず、

その上、所望の形状を自由に得ることができないという課題もあった。

【0013】

【発明の目的】本発明は、前記課題を解消せんとして成されたもので、その目的は、高電流放電時の静電容量に対する低電流放電時の静電容量の容量比が大きく、かつ低電流放電時も高電流放電時にも実用的な静電容量を有し、所望の形状を自由に得ることができる良好な成形性を有し、機械的強度の大きい耐久性に優れた補助電源用各種電池の電極用をはじめ、各種用途に適用可能な固形状活性炭と、それを分極性電極として用いた実用的な電気二重層コンデンサを提供することにある。

【0014】

【課題を解決するための手段】本発明者等は前記課題に対して鋭意研究の結果、耐久性や機械的強度を損なわない範囲で比表面積を大きくした多孔質の各種活性炭材料と炭化性樹脂とカーボンブラックから成る混合物を成形し、該成形体を非酸化性雰囲気中で炭化一体化して電解液のイオン径以上の細孔径を有するように細孔分布を制御して得られた炭素質を主体とする分極性電極材料は、高電流放電時の静電容量に対する低電流放電時の静電容量の容量比を大きくすることができ、低電流放電時にも、高電流放電時にも実用的な静電容量を有すると共に、成形性は勿論、機械的強度や耐久性に優れた固形状活性炭が得られることを見だし、本発明に至った。

【0015】即ち、本発明の固形状活性炭は、活性炭粉末及び／又は活性炭繊維等から成る炭素質を主体とする分極性電極材料と、それを100重量部とした時、0.5～10重量部の割合から成るカーボンブラックを含有してなるもので、300mA/cm²の高電流と30mA/cm²の低電流の定電流放電法で静電容量を測定した場合、前記高電流放電時の静電容量に対する低電流放電時の静電容量の容量比が40.0%以上であることを特徴とするものである。

【0016】また、前記固形状活性炭を分極性電極とした電気二重層コンデンサとして好適なものである。

【0017】

【作用】本発明の固形状活性炭は、活性炭粉末及び／又は活性炭繊維等から成る炭素質を主体とする分極性電極材料にカーボンブラックを所定量含有していることから、製造工程の炭化熱処理時に収縮率の差によって、得られた固形状活性炭は微小なクラックを有するものとなり、そのために該クラックが電気二重層を形成する電解液中のイオンが吸着することのできる細孔を増加させることになり、最終的に静電容量が向上するようになる。

【0018】その結果、低電流放電時の静電容量が大きく、更に高電流放電時と低電流放電時の静電容量の比も大で、バランスの取れた機械的強度及び耐久性にも優れた多目的の固形状活性炭とすることができる。

【0019】また、前記固形状活性炭を電気二重層コン

デンサの分極性電極とした場合、実用的な静電容量を有し、かつ電極の内部電気抵抗が低い、簡単な構造で効率の良い、耐久性に優れた小型の電気二重層コンデンサが得られる。

【0020】

【発明の実施の形態】以下、本発明の固形状活性炭及びそれを用いた電気二重層コンデンサについて詳述する。本発明の固形状活性炭は、活性炭粉末又は活性炭繊維、あるいは活性炭粉末及び活性炭繊維等から成る炭素質を主体とする分極性電極材料と、カーボンブラックと、バインダーとして添加される公知の炭化性樹脂を熱処理した炭化物とから成るものである。

【0021】本発明において、分極性電極材料100重量部に対するカーボンブラックの含有量が0.5重量部未満の場合には、電気二重層を形成する電解液中のイオンの電極への吸着性に変化はなく、得られた固形状活性炭の静電容量の向上に寄与せず、他方、前記カーボンブラックの含有量が10重量部を越えると、得られた固形状活性炭の強度が極端に低下してしまうことから0.5～10重量部に限定される。

【0022】また、前記カーボンブラックは、ガス状または液状の炭化水素を不完全燃焼させるか、あるいは1300℃前後で熱分解することによって得られる結晶化度が0.4～3.0程度の炭素で、数十nmから数百数十nm程度の粒子径を有し、それが集合して数千～数万nm程度の粒子集合体を形成しているものであり、例えばアセチレンブラックやケッチェンブラック等が代表例として挙げられる。

【0023】尚、前記結晶化度は、X線回折法において $2d \times \sin \theta = n\lambda$ で表される式で、dが38nm近傍の最強ピークの半値幅に対するベースからの該ピークの高さとの比から求めた値である。

【0024】一方、前記固形状活性炭は、300mA/cm²の高電流と30mA/cm²の低電流の定電流放電法で静電容量を測定した時、前記高電流放電時の静電容量に対する低電流放電時の静電容量の容量比が40.0%未満の場合には、用途が限定されてしまうため、多目的の固形状活性炭として適用できるということからは40.0%以上であることが必要である。

【0025】また、本発明の固形状活性炭は、その原料である活性炭粉末や活性炭繊維等として特に限定されるものではなく、ヤシ殻系や石炭系、木質系等のいずれでも良いが、コストと吸着能力の点ではヤシ殻系が最も望ましい。

【0026】尚、前記原料の活性炭粉末や活性炭繊維等は、目的とする静電容量によってその比表面積を選択すれば良く、得られた固形状活性炭を電気二重層コンデンサに用いる場合には、活性炭粉末では比表面積が1500～2500m²/g程度であるものが好適であり、また活性炭繊維では繊維径が6～18μmで比表面積が1

000~2500m²/g程度であるものが望ましく、それらは適宜混合して用いることも可能である。

【0027】次に、バインダーとして添加する炭化性樹脂は、公知の有機性樹脂であればいずれでも適用でき、特に限定するものではなく、例えば、フェノール又はテフロン、コールドール、ポリビニルブチラール(PVB)、ポリビニルホルマール(PVFM)等のポリビニルアセタール、酢酸ビニル等が挙げられ、とりわけ成形性あるいは得られる固形状活性炭の強度の点からは、ポリビニルブチラール(PVB)が最も望ましい。

【0028】更に、得られた固形状活性炭の比表面積は、原料の活性炭の比表面積によりその上限は規定されるが、比表面積が500m²/g未満では電解液と電極との界面に生じる電気二重層が少なくなるため、30mA/cm²の低電流で放電した時の静電容量が20F/cc未満となって実用的でない。

【0029】尚、前記固形状活性炭の比表面積が2000m²/gを越えると強度が低下する傾向があり、特に700~1500m²/g程度であれば静電容量及び強度という点からはより望ましく、更に、得られた固形状活性炭は、製造工程中や電気二重層コンデンサの分極性電極としての組み込み時に欠けや割れ等の破損を生じないためにも、少なくとも300g/mm²以上の強度を有するものが望ましい。

【0030】従って、前述のような固形状活性炭であれば、充分な静電容量が維持できると共に、機械的強度も確保でき、特に電気二重層コンデンサの分極性電極として最適なものである。

【0031】次に、本発明の固形状活性炭の製造方法の一例を述べる。活性炭粉末及び/又は活性炭繊維等の炭素質原料を主体とする分極性電極材料100重量部に対して、フェノール又はテフロン、コールドール、ポリビニルブチラール(PVB)等の公知の炭化性樹脂の少なくとも一種を20~200重量部、及びカーボンブラックを0.5~10重量部の割合で混合し、該混合物から泥漿又は造粒体を調製して成形用材料を調製する。

【0032】その後、得られた成形用材料を用いてドクターブレード法やテープ成形法、又は加圧成形法やロール成形法、押し出し成形法、あるいはそれらを組み合わせた成形法等の公知の成形法で所定形状に成形した成形体を、炭化熱処理して該成形体中の炭化性樹脂を炭化すると共に、前記活性炭粉末及び/又は活性炭繊維等の炭素質原料を主体とする分極性電極材料とカーボンブラックと炭化性樹脂の炭化物とを焼成一体化して固形状活性炭を得る。

【0033】前記炭化熱処理温度は、炭化性樹脂の炭化を十分に進行させると共に、活性炭粉末や活性炭繊維のネック部の焼結を進行させて充分な強度を保持させるためには、非酸化性雰囲気下で600~1200℃程度の温度が望ましく、特に700~900℃の温度が最適で

ある。

【0034】従って、前記炭化熱処理温度は、その温度を高くしたり、炭化時間を長くすれば強度は向上するものの、比表面積が減少してしまうため、用途に合わせて強度と静電容量との兼ね合いから、最適な細孔分布を有するように炭化熱処理条件を選択することが肝要である。

【0035】尚、本発明の固形状活性炭は、ドクターブレード法やカレンダーロール法等によりシート状に成形して活性炭基板としたり、各種プレス成形法でブロック状に成形したり、あるいは押出成形法により棒状や筒状としたり、それらを組み合わせたりして様々な形状とすることができる。

【0036】更に、前記シート状成形体を複数枚積層した後、非酸化性雰囲気下で熱処理することも可能であり、複数のシート状成形体を積層して熱圧着したり、あるいは密着液や接着剤等で接合することにより、互いの反り方向を相殺して熱処理時の反りの発生を低減することも可能となる。

【0037】

【実施例】本発明の固形状活性炭及びそれを用いた電気二重層コンデンサを以下のようにして評価した。先ず、BET値が2000m²/gのヤシ殻活性炭粉末100重量部に対して、PVBを90重量部と種類の異なるカーボンブラックを用い表1に示す割合で調合して高速混合攪拌機にて攪拌混合し、得られた造粒体を40メッシュの篩いで篩別して成形用原料を作製した。

【0038】次に、得られた成形用原料をプレス成形、あるいはロール成形して平板状の成形体を得た後、該成形体を大気中、エージング条件として200℃の温度で48時間保持する熱処理を行い、次いで真空中、800℃の温度で10分間保持する処理条件で炭化熱処理を行い、PVBを炭化させて活性炭とカーボンブラックの複合体である縦70mm、横50mm、厚さ1mmの評価用の活性炭基板を作製した。

【0039】次に、評価用の活性炭基板を電極とし、電解液中、それぞれ0.9Vの電圧で30分間充電した後、30mA/cm²と300mA/cm²の定電流放電法にて電極単位体積当たりの静電容量(F/cc)を求め、300mA/cm²の高電流放電時の静電容量に対する30mA/cm²の低電流放電時の静電容量の容量比を算出した。

【0040】また、前記活性炭基板の機械的強度の評価は、厚さ1mm、幅4mm、長さ40mmの試験片を用いて支点間距離を30mmとし、クロスヘッドスピードを0.5mm/min.として破断荷重から算出した。

【0041】次に、成形性の評価としては、前記活性炭基板を成形した時の造粒体の潰れ状態及び離型性について観察して判定した。

【0042】尚、活性炭基材に炭素化合物から成る有機

溶剤を含浸させ、更にバインダーを添加して作製した活性炭試料を比較例とした。 * 【0043】

* 【表1】

| 試料 番号 | カーボン ブラック 重量部 | 静電容量(F/CC) | | 容量比 B/A ×100 (%) | 機械的 強度 g/mm ² | 成形性 | 備 考 |
|----------|---------------------|-------------------|-------------------|---------------------------|--------------------------------|-----|----------|
| | | 低電流 放 電 (A) | 高電流 放 電 (B) | | | | |
| * 1 | — | 28.7 | 5.0 | 16.8 | 662 | 可 | |
| 2 | 0.5 | 35.5 | 17.6 | 49.6 | 631 | 良 | ケチエンブラック |
| 3 | 1.0 | 36.0 | 18.3 | 50.8 | 618 | 優 | " |
| 4 | 2.0 | 36.9 | 19.6 | 53.1 | 592 | " | " |
| 5 | 3.0 | 37.8 | 21.0 | 55.6 | 566 | " | " |
| 6 | 5.0 | 40.2 | 24.7 | 61.4 | 482 | 良 | " |
| 7 | 8.0 | 42.5 | 28.1 | 68.1 | 388 | " | " |
| 8 | 10.0 | 43.0 | 29.5 | 68.6 | 325 | " | " |
| * 9 | 15.0 | 46.1 | 36.3 | 78.7 | 96 | 不 良 | " |
| 10 | 0.5 | 30.5 | 12.3 | 40.3 | 647 | 良 | アセレンブラック |
| 11 | 1.0 | 31.3 | 12.8 | 40.9 | 634 | 優 | " |
| 12 | 2.0 | 31.9 | 13.5 | 42.3 | 608 | " | " |
| * 13 | — | 21.3 | 4.5 | 21.1 | 153 | 不 良 | 比較例 |

*印を付した試料番号は本発明の請求範囲外のものである。

【0044】表から明らかなように、比較例の試料番号13は、静電容量が低電流放電でも21.3F/ccであり、高電流放電では4.5F/ccと極めて低くなっており、容量比も21.1%と極めて不十分なものであり、本発明の請求範囲外であるカーボンブラックを含有しないものも同程度の特性を有するものであり、またカーボンブラックの含有量が10重量部を越える試料番号9では、静電容量や容量比は満足するものの、成形性が極めて悪く、機械的強度が劣り実用性に欠けるものである。

【0045】それらに対して、本発明では、いずれも静電容量及び容量比を満足すると共に、機械的強度も高く、成形性も良好なものであることが確認された。

【0046】尚、本発明は前記実施例に限定されるものではなく、本発明の主旨を満足するものであれば良いことはいふまでもない。

【0047】

※

※【発明の効果】以上詳述したように、本発明の固形状活性炭及びそれを用いた電気二重層コンデンサによれば、比表面積が大で静電容量を大きく向上させることができると共に、機械的強度の大きな耐久性に優れた各種用途に適用可能な多目的の固形状活性炭が得られ、静電容量に対する体積の小型化が実現できる。

【0048】従って、本発明の固形状活性炭を分極性電極として使用した場合には、電極として電解液に接する表面積が増大し、固形状活性炭の細孔に電解液のイオンが数多く吸着されるため、高電流放電時の静電容量が大きく、高電流放電時の静電容量に対する低電流放電時の静電容量の容量比も大きくなり、実用的な静電容量を有する簡単な構造で効率の良い、優れた小型の電気二重層コンデンサを得ることができる他、機械的強度にも優れた耐久性に富む補助電源用各種電池の電極用等、各種用途に好適な多目的の固形状活性炭が得られる。

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE
INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]Carbon black of 0.5 to 10 weight section is contained to polarizable electrode material 100 weight section which makes carbonaceous a subject. Solid form active carbon characterized by a capacity factor of electric capacity at the time of low current discharge to electric capacity at the time of said high-electric-current discharge being not less than 40.0% when electric capacity is measured by a constant-current-discharge method of high electric current of 300mA[cm]², and low current of 30 mA/cm².

[Claim 2]An electric double layer capacitor using the solid form active carbon according to claim 1 as a polarizable electrode.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] In this invention, an electric double layer capacitor and small mass capacitors including a lithium ion battery, It is related with the solid form active carbon which can generally be widely applied as a porous activated carbon sintered compact used for the filtering medium the electrode material used for various cells, such as a backup power supply, a power supply for vehicles, and auxiliary power, or a gas adsorption agent and the object for waterworks, for foodstuffs refining, and for wastewater purification, etc., and the electric double layer capacitor using it.

Therefore, it is related with the solid form active carbon which makes realizable the power storage system for electric power with especially large electric capacity and a big energy density, and the electric double layer capacitor using it as a polarizable electrode.

[0002]

[Description of the Prior Art] In recent years, although application to the various applicable fields which paid their attention to the characteristic is considered, especially, said activated carbon attracts attention as a porous carbon material a small mass capacitor and for the electrode materials of various cells, and examination has accomplished activated carbon variously.

[0003] The polarizable electrode which makes carbonaceous including said activated carbon a subject especially, It is used abundantly as an object for electric double layer capacitors which made the electrolyte intervene between these polarizable electrodes, and used the electric double layer formed by both interface and which has the electric capacity which attains to one 1000 times the number per unit volume of this as compared with the conventional capacitor.

[0004] The demand is quickly extended with development of the electronics field -- this electric double layer capacitor is applied to auxiliary power, such as a small memory backup power supply and a mass motor, from having a function of both a capacitor and a cell.

[0005] As said electrode material, the solid form active carbon of the porosity generally applied widely is used, and at the beginning as such solid form active carbon, For example, what kneaded organic resin, such as carbonaceous of activated carbon etc., tetrafluoroethylene resin or a fluorine polymer, and was fabricated by publicly known molding means, such as roll diffusion bonding and compression forming, to the sheet shaped was used.

[0006] However, as an electrode material of the above capacitors or a cell, In order to satisfy the performance of especially high electric capacity and low internal resistance and to satisfy the demand of a miniaturization of the electronic parts of these days, That it is hard to cause a crack, breakage, etc. with the porous body structure in consideration of the minimization of volume to prescribed capacity and the impregnating ability of the electrolysis solution, etc. to excel in endurance and a mechanical property further also as the general characteristic, etc. have come to be demanded.

[0007] In order to satisfy said many demands, then, active carbon particles or carbon particulates, and carbon fiber, Or mix and carry out pressure sintering of activated carbon powder, the mesophase system carbon, etc., or, Or after forming membranes on the substrate and heat-treating the mixture made to dissolve activated carbon powder and powdered phenol resin in an organic solvent in a non-oxidizing atmosphere after heat cure, the solid form active carbon by various manufacturing methods, such as carrying out activation treatment, was proposed.

[0008]However, this solid form active carbon is manufactured from the mixture of the activated carbon of the porosity which enlarged specific surface area in the range which spoils neither endurance nor a mechanical strength, and said organic resin, The fill ration of this activated carbon is restrained from a relation with whole pore volume in a fixed range, and moreover said organic resin with a good moldability, A possibility of closing the micropore of activated carbon is high, specific surface area decreases further conjointly and the fill ration of said activated carbon satisfies neither from the point of the minimization of volume to said electric capacity.

[0009]On the other hand, when organic resin of the hyperviscosity which does not close the micropore of said activated carbon was used, since the moldability was bad, there was a fault that the mechanical strength after carbonization heat treatment was also very low.

[0010]Since it impregnates with organic solvents which change from carbon compounds to an activated carbon substrate, such as alkanes, alkenes, and alcohol, in order to solve this problem, the method of carrying out addition mixing of the binder which comprises organic resin, and manufacturing an activated carbon electrode, etc. are proposed (refer to JP,8-138979,A).

[0011]

[Problem(s) to be Solved by the Invention]However, when said activated carbon electrode measures the electric capacity by a constant-current-discharge method, If it is lower than the electric capacity predicted from the rate of activated carbon and various organic resin or discharges by the low current about 30 mA/cm^2 , even if about 20 F/cc of electric capacity will be obtained, Conversely, when it discharges by the high electric current about 300 mA/cm^2 , electric capacity is very low in about five F/cc and], There are some to which the capacity factor of the electric capacity at the time of the low current discharge to the electric capacity at the time of high-electric-current discharge becomes low with about 20%, For example, although it could apply as an object for the polarizable electrodes of an electric double layer capacitor, the technical problem that it could not apply to the use which needs the electric capacity at the time of high-electric-current discharge, but a use was limited, and auxiliary power, such as a motor, etc. could not be adopted as multiple-purpose solid form active carbon occurred.

[0012]With the manufacturing method of said activated carbon electrode, by organic solvents, such as alkanes and alkenes, in order not to plasticize, the technical problem that the easy Plastic solid of handling with a hard granulated body was not acquired, and desired shape moreover could not be obtained freely also occurred.

[0013]

[Objects of the Invention]Accomplished this invention as a dissolution plug and said technical problem the purpose, The capacity factor of the electric capacity at the time of the low current discharge to the electric capacity at the time of high-electric-current discharge is large, And have electric capacity practical also at the time of high-electric-current discharge also at the time of low current discharge, and it has a good moldability which can obtain desired shape freely, The object for the electrodes of the various cells for auxiliary power excellent in endurance with a large mechanical strength is begun, and it is in providing solid form active carbon applicable to a various application, and the practical electric double layer capacitor using it as a polarizable electrode.

[0014]

[Means for Solving the Problem]This invention persons fabricate wholeheartedly a mixture which comprises various activated carbon materials, carbonization nature resin, and carbon black of porosity which enlarged specific surface area in the range which spoils neither endurance nor a mechanical strength to said technical problem as a result of research, Polarizable electrode material which makes a subject carbonaceous acquired by controlling pore distribution so that the carbonization unification of this Plastic solid might be carried out in a non-oxidizing atmosphere and it might have a pole diameter more than a diameter of ion of an electrolysis solution, Could enlarge a capacity factor of electric

capacity at the time of low current discharge to electric capacity at the time of high-electric-current discharge, and it had electric capacity practical at the time of low current discharge and high-electric-current discharge, and it found out that solid form active carbon excellent in a mechanical strength or endurance was obtained as well as a moldability, and resulted in this invention.

[0015]Namely, polarizable electrode material in which solid form active carbon of this invention makes a subject carbonaceous which comprises activated carbon powder, an activated carbon fiber, etc., When it is made into 100 weight sections, it is a thing containing carbon black which comprises a rate of 0.5 to 10 weight section, When electric capacity is measured by a constant-current-discharge method of high electric current of 300 mA/cm^2 , and low current of 30 mA/cm^2 , it is characterized by a capacity factor of electric capacity at the time of low current discharge to electric capacity at the time of said high-electric-current discharge being not less than 40.0%.

[0016]It is suitable as an electric double layer capacitor which used said solid form active carbon as a polarizable electrode.

[0017]

[Function]Since the solid form active carbon of this invention is carrying out specified quantity content of the carbon black at the polarizable electrode material which makes a subject carbonaceous which comprises activated carbon powder, an activated carbon fiber, etc., at the time of carbonization heat treatment of a manufacturing process according to the difference of contraction. The obtained solid form active carbon makes the fine pores which can stick to the ion in the electrolysis solution in which it becomes what has a minute crack, therefore this crack forms an electric double layer increased, and its electric capacity comes to improve eventually.

[0018]As a result, the electric capacity at the time of low current discharge is large, and also the ratio of the electric capacity at the time of high-electric-current discharge and low current discharge can also be used as multiple-purpose solid form active carbon excellent also in the mechanical strength and endurance which maintained balance in size.

[0019]When said solid form active carbon is used as the polarizable electrode of an electric double layer capacitor, the small electric double layer capacitor has practical electric capacity and the inner electrical resistance of the electrode excelled [electric double layer capacitor] in efficient endurance with an easy low structure is obtained.

[0020]

[Embodiment of the Invention]Hereafter, the solid form active carbon of this invention and the electric double layer capacitor using it are explained in full detail. The solid form active carbon of this invention comprises the polarizable electrode material which makes a subject carbonaceous which comprises activated carbon powder, an activated carbon fiber or activated carbon powder, an activated carbon fiber, etc., carbon black, and the carbide which heat-treated the publicly known carbonization nature resin added as a binder.

[0021]In this invention, when the content of carbon black to polarizable electrode material 100 weight section is less than 0.5 weight sections, If it does not contribute to improvement in the electric capacity of the solid form active carbon obtained by being changeless to the adsorptivity to the electrode of the ion in the electrolysis solution which forms an electric double layer but the content of another side and said carbon black exceeds ten weight sections, Since the intensity of the obtained solid form active carbon falls extremely, it is limited to 0.5 to 10 weight section.

[0022]Said carbon black is carbon whose degree of crystallinity obtained by carrying out the incomplete combustion of the gaseous or liquefied hydrocarbon, or carrying out a pyrolysis at around 1300°C is 0.4 to about 3.0, It has the particle diameter of about 10 nm more than 100 from tens of nm, they gather, and thousands - the particle aggregate of about 10,000 nm of numbers are formed. For example, acetylene black, Ketchen black, etc. are mentioned as an example of representation.

[0023]Said degree of crystallinity is a formula expressed with $2 d \sin \theta = n \lambda$ in an X-ray

diffraction method, and d is the value calculated from the ratio with the height of this peak from the base to the half breadth of an about 38-nm strongest peak.

[0024]When said solid form active carbon measures electric capacity on the other hand by the constant-current-discharge method of the high electric current of 300 mA/cm^2 , and the low current of 30 mA/cm^2 , Since a use will be limited when the capacity factor of the electric capacity at the time of the low current discharge to the electric capacity at the time of said high-electric-current discharge is less than 40.0%, and it says that it is applicable as multiple-purpose solid form active carbon, it is required to be not less than 40.0%.

[0025]Although the solid form active carbon of this invention may not be limited as [the activated carbon powder which is the raw material, an activated carbon fiber, etc.] especially and any, such as a coconut husks system, a Carboniferous system, a woody system, may be sufficient as it, in respect of cost and adsorption capability, its coconut husks system is the most desirable.

[0026]Activated carbon powder, an activated carbon fiber, etc. of said raw material, In using for an electric double layer capacitor the solid form active carbon obtained with the target electric capacity by what is necessary being just to choose the specific surface area, That whose specific surface area is a $1500\text{-}2500 \text{ m}^2/\text{g}$ grade in activated carbon powder is preferred, and it is also possible for that whose specific surface area a fiber diameter is a $1000\text{-}2500 \text{ m}^2/\text{g}$ grade in 6-18 micrometers to be desirable, to mix them suitably, and to use at an activated carbon fiber.

[0027]Next, the carbonization nature resin added as a binder, It is not what can apply either if it is publicly known organic nature resin, and is limited especially, For example, phenol or Teflon, coal tar, a polyvinyl butyral (PVB), Polyvinyl acetals, such as a polyvinyl formal (PVFM), vinyl acetate, etc. are mentioned, and a polyvinyl butyral (PVB) is especially the most desirable from a point of a moldability or the intensity of the solid form active carbon obtained.

[0028]Although the maximum is prescribed by the specific surface area of the activated carbon of a raw material, the specific surface area of the obtained solid form active carbon, Since the electric double layer which specific surface area produces in the interface of an electrolysis solution and an electrode in less than $500 \text{ m}^2/\text{g}$ decreases, electric capacity when it discharges by the low current of 30 mA/cm^2 becomes in less than 20 F/cc and], and is not practical.

[0029]There is a tendency for intensity to fall if the specific surface area of said solid form active carbon exceeds $2000 \text{ m}^2/\text{g}$, Solid form active carbon more desirable especially from the point of [if it is a $700\text{-}1500 \text{ m}^2/\text{g}$ grade] electric capacity and intensity and obtained further, Also in order not to produce breakage of a chip, a crack, etc. at the time of the inclusion as a polarizable electrode of the inside of a manufacturing process, or an electric double layer capacitor, what has the intensity more than at least 300 g/mm^2 is desirable.

[0030]Therefore, if it is the above solid form active carbon, sufficient electric capacity is maintainable, and a mechanical strength can also be secured and it is the optimal especially as a polarizable electrode of an electric double layer capacitor.

[0031]Next, an example of the manufacturing method of the solid form active carbon of this invention is described. As opposed to polarizable electrode material 100 weight section which makes a subject carbonaceous raw materials, such as activated carbon powder and/or an activated carbon fiber, publicly known carbonization nature resin, such as phenol or Teflon, coal tar, and a polyvinyl butyral (PVB), -- at least, a kind is mixed by 20 to 200 weight section, carbon black is mixed at a rate of 0.5 to 10 weight section, slurry or a granulated body is prepared from this mixture, and the charge of shaping material is prepared.

[0032]Using the obtained charge of shaping material, then, a doctor blade method and a tape-forming method, Or carry out carbonization heat treatment of the Plastic solid fabricated by the molding method with publicly known compression moulding technique, roll diffusion bonding and an extrusion-

molding method, or molding method that combined them etc. to specified shape, and carbonize carbonization nature resin in this Plastic solid, and. The calcination unification of the polarizable electrode material and carbon black which make a subject carbonaceous raw materials, such as said activated carbon powder and/or an activated carbon fiber, and the carbide of carbonization nature resin is carried out, and solid form active carbon is obtained.

[0033]In order for said carbonization heat treatment temperature to fully advance carbonization of carbonization nature resin, and to advance sintering of the neck part of activated carbon powder or an activated carbon fiber and to make sufficient intensity hold, its temperature of about 600-1200 ** is desirable under a non-oxidizing atmosphere, and its temperature which is 700-900 ** is especially the optimal.

[0034]Therefore, if said carbonization heat treatment temperature makes the temperature high or carbonization time is lengthened, although intensity will improve, since specific surface area decreases, it is important to choose a carbonization heat treatment condition from the balance of intensity and electric capacity according to a use, so that it may have the optimal pore distribution.

[0035]Fabricate the solid form active carbon of this invention to a sheet shaped by doctor blade method, the calendering roll method, etc., and consider it as activated carbon boards, or, It can be considered as various shape, and combining them. [fabricating by various press-forming methods to block like shape] [considering it as rod form or tubed by an extrusion method]

[0036]By heat-treating under a non-oxidizing atmosphere being also possible, and laminating and bonding two or more sheet-shaped Plastic solids by thermo-compression, or joining with adhesion liquid, adhesives, etc., after laminating two or more sheets of said sheet-shaped Plastic solid, It also becomes possible to offset the mutual direction of curvature and to reduce generating of the curvature at the time of heat treatment.

[0037]

[Example]The solid form active carbon of this invention and the electric double layer capacitor using it were evaluated as follows. First, a BET value receives coconut husks activated-carbon-powder 100 weight section of 2000 m²/g, PVB was prepared at a rate shown in Table 1 using the carbon black from which 90 weight sections and a kind differ, the screen exception carried out the granulated body obtained by carrying out agitation mixing with the high-speed agitation mix machine with the sieve of 40 meshes, and the raw material for shaping was produced.

[0038]The obtained raw material for shaping Next, after [press forming or after carrying out roll forming and acquiring a plate-like Plastic solid], Heat treatment which holds this Plastic solid at the temperature of 200 ** as aging conditions among the atmosphere for 48 hours is performed, Subsequently, carbonization heat treatment was performed among the vacuum by the processing condition held for 10 minutes at the temperature of 800 **, PVB was carbonized and the activated carbon boards for evaluation (70 mm long which are activated carbon and a complex of carbon black, the side of 50 mm, and 1 mm in thickness) were produced.

[0039]Next, after using the activated carbon boards for evaluation as an electrode and charging for 30 minutes on the voltage of 0.9V among an electrolysis solution, respectively, The electric capacity per electrode unit volume (F/cc) was calculated by the constant-current-discharge method of 30 mA/cm² and 300 mA/cm², and the capacity factor of the electric capacity at the time of low current discharge of 30 mA/cm² to the electric capacity at the time of high-electric-current discharge of 300 mA/cm² was computed.

[0040]Evaluation of the mechanical strength of said activated carbon boards set distance between fulcrums to 30 mm using a specimen 1 mm in thickness, 4 mm in width, and 40 mm in length, made crosshead speed 0.5mm/min., and computed it from breaking load.

[0041]Next, as evaluation of a moldability, the crushing state and mold-release characteristic of the granulated body when said activated carbon boards were fabricated were observed and judged.

[0042]It impregnated with the organic solvent which changes from carbon compounds to an activated carbon substrate, and also the activated carbon sample which added and produced the binder was made into the comparative example.

[0043]

[Table 1]

| 試料 番号 | カーボン ブラック 重量部 | 静電容量(F/CC) | | 容量比 B/A ×100 (%) | 機械的 強度 g/mm ² | 成形性 | 備 考 |
|----------|---------------------|-------------------|-------------------|---------------------------|--------------------------------|-----|----------|
| | | 低電流 放 電 (A) | 高電流 放 電 (B) | | | | |
| * 1 | — | 29.7 | 5.0 | 16.8 | 662 | 可 | |
| 2 | 0.5 | 35.5 | 17.6 | 49.6 | 631 | 良 | ケチエンブラック |
| 3 | 1.0 | 36.0 | 18.3 | 50.8 | 618 | 優 | " |
| 4 | 2.0 | 36.9 | 19.6 | 53.1 | 592 | " | " |
| 5 | 3.0 | 37.8 | 21.0 | 55.6 | 566 | " | " |
| 6 | 5.0 | 40.2 | 24.7 | 61.4 | 482 | 良 | " |
| 7 | 8.0 | 42.5 | 28.1 | 66.1 | 388 | " | " |
| 8 | 10.0 | 43.0 | 29.5 | 68.6 | 325 | " | " |
| * 9 | 15.0 | 46.1 | 36.3 | 78.7 | 96 | 不 良 | " |
| 10 | 0.5 | 30.5 | 12.3 | 40.3 | 647 | 良 | アセチンブラック |
| 11 | 1.0 | 31.3 | 12.8 | 40.9 | 634 | 優 | " |
| 12 | 2.0 | 31.9 | 13.5 | 42.3 | 608 | " | " |
| * 13 | — | 21.3 | 4.5 | 21.1 | 153 | 不 良 | 比較例 |

*印を付した試料番号は本発明の請求範囲外のものである。

[0044]The sample number 13 of a comparative example is 21.3 F/cc in electric capacity also low current discharge so that clearly from a table.

Are very low in 4.5 F/[cc and], and the high-electric-current discharge of a capacity factor is very as insufficient as 21.1%, In the sample number 9 in which what does not contain carbon black which is outside the generic claim of this invention has the comparable characteristic, and the content of carbon black exceeds ten weight sections for it. Although electric capacity and a capacity factor are satisfied, a moldability is very bad, a mechanical strength is inferior, and practicality is missing.

[0045]Each was satisfied with this invention of electric capacity and a capacity factor to them, and it was checked that a mechanical strength is also high and a moldability is also good.

[0046]Things cannot be overemphasized that this invention should just be what is not limited to said example and satisfies the main point of this invention.

[0047]

[Effect of the Invention]As explained in full detail above, according to the solid form active carbon of this invention, and the electric double layer capacitor using it, specific surface area can raise electric capacity greatly in size, and. Multiple-purpose solid form active carbon applicable to the various application excellent in endurance with a big mechanical strength is obtained, and the miniaturization of volume to electric capacity can be realized.

[0048]Therefore, when the solid form active carbon of this invention is used as a polarizable electrode. Since the surface area which touches an electrolysis solution as an electrode increases and the fine pores of solid form active carbon are adsorbed in many ion of an electrolysis solution, The electric capacity at the time of high-electric-current discharge is large, and the capacity factor of the electric capacity at the time of the low current discharge to the electric capacity at the time of high-electric-current discharge also becomes large, The efficient outstanding small electric double layer capacitor

can be obtained with an easy structure of having practical electric capacity, and also the suitable multiple-purpose solid form active carbon for various applications, such as an object for the electrodes of the various cells for auxiliary power which are rich in the endurance excellent also in the mechanical strength, is obtained.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention]In this invention, an electric double layer capacitor and small mass capacitors including a lithium ion battery, It is related with the solid form active carbon which can generally be widely applied as a porous activated carbon sintered compact used for the filtering medium the electrode material used for various cells, such as a backup power supply, a power supply for vehicles, and auxiliary power, or a gas adsorption agent and the object for waterworks, for foodstuffs refining, and for wastewater purification, etc., and the electric double layer capacitor using it. Therefore, it is related with the solid form active carbon which makes realizable the power storage system for electric power with especially large electric capacity and a big energy density, and the electric double layer capacitor using it as a polarizable electrode.

[Translation done.]

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PRIOR ART

[Description of the Prior Art]In recent years, although application to the various applicable fields which paid their attention to the characteristic is considered, especially, said activated carbon attracts attention as a porous carbon material a small mass capacitor and for the electrode materials of various cells, and examination has accomplished activated carbon variously.

[0003]The polarizable electrode which makes carbonaceous including said activated carbon a subject especially, It is used abundantly as an object for electric double layer capacitors which made the electrolyte intervene between these polarizable electrodes, and used the electric double layer formed by both interface and which has the electric capacity which attains to one 1000 times the number per unit volume of this as compared with the conventional capacitor.

[0004]The demand is quickly extended with development of the electronics field -- this electric double layer capacitor is applied to auxiliary power, such as a small memory backup power supply and a mass motor, from having a function of both a capacitor and a cell.

[0005]As said electrode material, the solid form active carbon of the porosity generally applied widely is used, and at the beginning as such solid form active carbon, For example, what kneaded organic resin, such as carbonaceous of activated carbon etc., tetrafluoroethylene resin or a fluorine polymer, and was fabricated by publicly known molding means, such as roll diffusion bonding and compression forming, to the sheet shaped was used.

[0006]However, as an electrode material of the above capacitors or a cell, In order to satisfy the performance of especially high electric capacity and low internal resistance and to satisfy the demand of a miniaturization of the electronic parts of these days, That it is hard to cause a crack, breakage, etc. with the porous body structure in consideration of the minimization of volume to prescribed capacity and the impregnating ability of the electrolysis solution, etc. to excel in endurance and a mechanical property further also as the general characteristic, etc. have come to be demanded.

[0007]In order to satisfy said many demands, then, active carbon particles or carbon particulates, and carbon fiber, Or mix and carry out pressure sintering of activated carbon powder, the mesophase system carbon, etc., or, Or after forming membranes on the substrate and heat-treating the mixture made to dissolve activated carbon powder and powdered phenol resin in an organic solvent in a non-oxidizing atmosphere after heat cure, the solid form active carbon by various manufacturing methods, such as carrying out activation treatment, was proposed.

[0008]However, this solid form active carbon is manufactured from the mixture of the activated carbon of the porosity which enlarged specific surface area in the range which spoils neither endurance nor a mechanical strength, and said organic resin, The fill ration of this activated carbon is restrained from a relation with whole pore volume in a fixed range, and moreover said organic resin with a good moldability, A possibility of closing the micropore of activated carbon is high, specific surface area decreases further conjointly and the fill ration of said activated carbon satisfies neither from the point of the minimization of volume to said electric capacity.

[0009]On the other hand, when organic resin of the hyperviscosity which does not close the micropore of said activated carbon was used, since the moldability was bad, there was a fault that the mechanical strength after carbonization heat treatment was also very low.

[0010]Since it impregnates with organic solvents which change from carbon compounds to an activated carbon substrate, such as alkanes, alkenes, and alcohol, in order to solve this problem, the method of carrying out addition mixing of the binder which comprises organic resin, and manufacturing an activated carbon electrode, etc. are proposed (refer to JP,8-138979,A).

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EFFECT OF THE INVENTION

[Effect of the Invention]As explained in full detail above, according to the solid form active carbon of this invention, and the electric double layer capacitor using it, specific surface area can raise electric capacity greatly in size, and. Multiple-purpose solid form active carbon applicable to the various application excellent in endurance with a big mechanical strength is obtained, and the miniaturization of volume to electric capacity can be realized.

[0048]Therefore, when the solid form active carbon of this invention is used as a polarizable electrode. Since the surface area which touches an electrolysis solution as an electrode increases and the fine pores of solid form active carbon are adsorbed in many ion of an electrolysis solution, The electric capacity at the time of high-electric-current discharge is large, and the capacity factor of the electric capacity at the time of the low current discharge to the electric capacity at the time of high-electric-current discharge also becomes large, The efficient outstanding small electric double layer capacitor can be obtained with an easy structure of having practical electric capacity, and also the suitable multiple-purpose solid form active carbon for various applications, such as an object for the electrodes of the various cells for auxiliary power which are rich in the endurance excellent also in the mechanical strength, is obtained.

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MEANS

[Means for Solving the Problem]This invention persons fabricate wholeheartedly a mixture which comprises various activated carbon materials, carbonization nature resin, and carbon black of porosity which enlarged specific surface area in the range which spoils neither endurance nor a mechanical strength to said technical problem as a result of research, Polarizable electrode material which makes a subject carbonaceous acquired by controlling pore distribution so that the carbonization unification of this Plastic solid might be carried out in a non-oxidizing atmosphere and it might have a pole diameter more than a diameter of ion of an electrolysis solution, Could enlarge a capacity factor of electric capacity at the time of low current discharge to electric capacity at the time of high-electric-current discharge, and it had electric capacity practical at the time of low current discharge and high-electric-current discharge, and it found out that solid form active carbon excellent in a mechanical strength or endurance was obtained as well as a moldability, and resulted in this invention.

[0015]Namely, polarizable electrode material in which solid form active carbon of this invention makes a subject carbonaceous which comprises activated carbon powder, an activated carbon fiber, etc., When it is made into 100 weight sections, it is a thing containing carbon black which comprises a rate of 0.5

to 10 weight section, When electric capacity is measured by a constant-current-discharge method of high electric current of 300 mA/cm², and low current of 30 mA/cm², it is characterized by a capacity factor of electric capacity at the time of low current discharge to electric capacity at the time of said high-electric-current discharge being not less than 40.0%.

[0016]It is suitable as an electric double layer capacitor which used said solid form active carbon as a polarizable electrode.

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OPERATION

[Function]Since the solid form active carbon of this invention is carrying out specified quantity content of the carbon black at the polarizable electrode material which makes a subject carbonaceous which comprises activated carbon powder, an activated carbon fiber, etc., at the time of carbonization heat treatment of a manufacturing process according to the difference of contraction. The obtained solid form active carbon makes the fine pores which can stick to the ion in the electrolysis solution in which it becomes what has a minute crack, therefore this crack forms an electric double layer increased, and its electric capacity comes to improve eventually.

[0018]As a result, the electric capacity at the time of low current discharge is large, and also the ratio of the electric capacity at the time of high-electric-current discharge and low current discharge can also be used as multiple-purpose solid form active carbon excellent also in the mechanical strength and endurance which maintained balance in size.

[0019]When said solid form active carbon is used as the polarizable electrode of an electric double layer capacitor, the small electric double layer capacitor has practical electric capacity and the inner electrical resistance of the electrode excelled [electric double layer capacitor] in efficient endurance with an easy low structure is obtained.

[0020]

[Embodiment of the Invention]Hereafter, the solid form active carbon of this invention and the electric double layer capacitor using it are explained in full detail. The solid form active carbon of this invention comprises the polarizable electrode material which makes a subject carbonaceous which comprises activated carbon powder, an activated carbon fiber or activated carbon powder, an activated carbon fiber, etc., carbon black, and the carbide which heat-treated the publicly known carbonization nature resin added as a binder.

[0021]In this invention, when the content of carbon black to polarizable electrode material 100 weight

section is less than 0.5 weight sections, If it does not contribute to improvement in the electric capacity of the solid form active carbon obtained by being changeless to the adsorptivity to the electrode of the ion in the electrolysis solution which forms an electric double layer but the content of another side and said carbon black exceeds ten weight sections, Since the intensity of the obtained solid form active carbon falls extremely, it is limited to 0.5 to 10 weight section.

[0022] Said carbon black is carbon whose degree of crystallinity obtained by carrying out the incomplete combustion of the gaseous or liquefied hydrocarbon, or carrying out a pyrolysis at around 1300 °C is 0.4 to about 3.0, It has the particle diameter of about 10 nm more than 100 from tens of nm, they gather, and thousands - the particle aggregate of about 10,000 nm of numbers are formed. For example, acetylene black, Ketchen black, etc. are mentioned as an example of representation.

[0023] Said degree of crystallinity is a formula expressed with $2d \sin \theta = n \lambda$ in an X-ray diffraction method, and d is the value calculated from the ratio with the height of this peak from the base to the half breadth of an about 38-nm strongest peak.

[0024] When said solid form active carbon measures electric capacity on the other hand by the constant-current-discharge method of the high electric current of 300 mA/cm², and the low current of 30 mA/cm², Since a use will be limited when the capacity factor of the electric capacity at the time of the low current discharge to the electric capacity at the time of said high-electric-current discharge is less than 40.0%, and it says that it is applicable as multiple-purpose solid form active carbon, it is required to be not less than 40.0%.

[0025] Although the solid form active carbon of this invention may not be limited as [the activated carbon powder which is the raw material, an activated carbon fiber, etc.] especially and any, such as a coconut husks system, a Carboniferous system, a woody system, may be sufficient as it, in respect of cost and adsorption capability, its coconut husks system is the most desirable.

[0026] Activated carbon powder, an activated carbon fiber, etc. of said raw material, In using for an electric double layer capacitor the solid form active carbon obtained with the target electric capacity by what is necessary being just to choose the specific surface area, That whose specific surface area is a 1500-2500 m²/g grade in activated carbon powder is preferred, and it is also possible for that whose specific surface area a fiber diameter is a 1000-2500 m²/g grade in 6-18 micrometers to be desirable, to mix them suitably, and to use at an activated carbon fiber.

[0027] Next, the carbonization nature resin added as a binder, It is not what can apply either if it is publicly known organic nature resin, and is limited especially, For example, phenol or Teflon, coal tar, a polyvinyl butyral (PVB), Polyvinyl acetals, such as a polyvinyl formal (PVFM), vinyl acetate, etc. are mentioned, and a polyvinyl butyral (PVB) is especially the most desirable from a point of a moldability or the intensity of the solid form active carbon obtained.

[0028] Although the maximum is prescribed by the specific surface area of the activated carbon of a raw material, the specific surface area of the obtained solid form active carbon, Since the electric double layer which specific surface area produces in the interface of an electrolysis solution and an electrode in less than 500 m²/g decreases, electric capacity when it discharges by the low current of 30 mA/cm² becomes in less than 20 F/[cc and], and is not practical.

[0029] There is a tendency for intensity to fall if the specific surface area of said solid form active carbon exceeds 2000 m²/g, Solid form active carbon more desirable especially from the point of [if it is a 700-1500 m²/g grade] electric capacity and intensity and obtained further, Also in order not to produce breakage of a chip, a crack, etc. at the time of the inclusion as a polarizable electrode of the inside of a manufacturing process, or an electric double layer capacitor, what has the intensity more than at least 300g/[mm]² is desirable.

[0030] Therefore, if it is the above solid form active carbon, sufficient electric capacity is maintainable,

and a mechanical strength can also be secured and it is the optimal especially as a polarizable electrode of an electric double layer capacitor.

[0031]Next, an example of the manufacturing method of the solid form active carbon of this invention is described. As opposed to polarizable electrode material 100 weight section which makes a subject carbonaceous raw materials, such as activated carbon powder and/or an activated carbon fiber, publicly known carbonization nature resin, such as phenol or Teflon, coal tar, and a polyvinyl butyral (PVB), -- at least, a kind is mixed by 20 to 200 weight section, carbon black is mixed at a rate of 0.5 to 10 weight section, slurry or a granulated body is prepared from this mixture, and the charge of shaping material is prepared.

[0032]Using the obtained charge of shaping material, then, a doctor blade method and a tape-forming method, Or carry out carbonization heat treatment of the Plastic solid fabricated by the molding method with publicly known compression moulding technique, roll diffusion bonding and an extrusion-molding method, or molding method that combined them etc. to specified shape, and carbonize carbonization nature resin in this Plastic solid, and. The calcination unification of the polarizable electrode material and carbon black which make a subject carbonaceous raw materials, such as said activated carbon powder and/or an activated carbon fiber, and the carbide of carbonization nature resin is carried out, and solid form active carbon is obtained.

[0033]In order for said carbonization heat treatment temperature to fully advance carbonization of carbonization nature resin, and to advance sintering of the neck part of activated carbon powder or an activated carbon fiber and to make sufficient intensity hold, its temperature of about 600-1200 ** is desirable under a non-oxidizing atmosphere, and its temperature which is 700-900 ** is especially the optimal.

[0034]Therefore, if said carbonization heat treatment temperature makes the temperature high or carbonization time is lengthened, although intensity will improve, since specific surface area decreases, it is important to choose a carbonization heat treatment condition from the balance of intensity and electric capacity according to a use, so that it may have the optimal pore distribution.

[0035]Fabricate the solid form active carbon of this invention to a sheet shaped by doctor blade method, the calendering roll method, etc., and consider it as activated carbon boards, or, It can be considered as various shape, and combining them. [fabricating by various press-forming methods to block like shape] [considering it as rod form or tubed by an extrusion method]

[0036]By heat-treating under a non-oxidizing atmosphere being also possible, and laminating and bonding two or more sheet-shaped Plastic solids by thermo-compression, or joining with adhesion liquid, adhesives, etc., after laminating two or more sheets of said sheet-shaped Plastic solid, It also becomes possible to offset the mutual direction of curvature and to reduce generating of the curvature at the time of heat treatment.

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[Embodiment of the Invention] Hereafter, the solid form active carbon of this invention and the electric double layer capacitor using it are explained in full detail. The solid form active carbon of this invention comprises the polarizable electrode material which makes a subject carbonaceous which comprises activated carbon powder, an activated carbon fiber or activated carbon powder, an activated carbon fiber, etc., carbon black, and the carbide which heat-treated the publicly known carbonization nature resin added as a binder.

[0021] In this invention, when the content of carbon black to polarizable electrode material 100 weight section is less than 0.5 weight sections, If it does not contribute to improvement in the electric capacity of the solid form active carbon obtained by being changeless to the adsorptivity to the electrode of the ion in the electrolysis solution which forms an electric double layer but the content of another side and said carbon black exceeds ten weight sections, Since the intensity of the obtained solid form active carbon falls extremely, it is limited to 0.5 to 10 weight section.

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[0030]Therefore, if it is the above solid form active carbon, sufficient electric capacity is maintainable, and a mechanical strength can also be secured and it is the optimal especially as a polarizable electrode of an electric double layer capacitor.

[0031]Next, an example of the manufacturing method of the solid form active carbon of this invention is described. As opposed to polarizable electrode material 100 weight section which makes a subject carbonaceous raw materials, such as activated carbon powder and/or an activated carbon fiber, publicly known carbonization nature resin, such as phenol or Teflon, coal tar, and a polyvinyl butyral (PVB), -- at least, a kind is mixed by 20 to 200 weight section, carbon black is mixed at a rate of 0.5 to 10 weight section, slurry or a granulated body is prepared from this mixture, and the charge of shaping material is prepared.

[0032]Using the obtained charge of shaping material, then, a doctor blade method and a tape-forming method, Or carry out carbonization heat treatment of the Plastic solid fabricated by the molding method with publicly known compression moulding technique, roll diffusion bonding and an extrusion-molding method, or molding method that combined them etc. to specified shape, and carbonize carbonization nature resin in this Plastic solid, and. The calcination unification of the polarizable electrode material and carbon black which make a subject carbonaceous raw materials, such as said activated carbon powder and/or an activated carbon fiber, and the carbide of carbonization nature resin is carried out, and solid form active carbon is obtained.

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[0035]Fabricate the solid form active carbon of this invention to a sheet shaped by doctor blade method, the calendaring roll method, etc., and consider it as activated carbon boards, or, It can be considered as various shape, and combining them. [fabricating by various press-forming methods to block like shape] [considering it as rod form or tubed by an extrusion method]

[0036]By heat-treating under a non-oxidizing atmosphere being also possible, and laminating and bonding two or more sheet-shaped Plastic solids by thermo-compression, or joining with adhesion liquid, adhesives, etc., after laminating two or more sheets of said sheet-shaped Plastic solid, It also becomes possible to offset the mutual direction of curvature and to reduce generating of the curvature at the time of heat treatment.

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EXAMPLE

[Example]The solid form active carbon of this invention and the electric double layer capacitor using it were evaluated as follows. First, a BET value receives coconut husks activated-carbon-powder 100 weight section of 2000 m²/g, PVB was prepared at a rate shown in Table 1 using the carbon black from which 90 weight sections and a kind differ, the screen exception carried out the granulated body obtained by carrying out agitation mixing with the high-speed agitation mix machine with the sieve of 40 meshes, and the raw material for shaping was produced.

[0038]The obtained raw material for shaping Next, after [press forming or after carrying out roll forming and acquiring a plate-like Plastic solid], Heat treatment which holds this Plastic solid at the temperature of 200 ** as aging conditions among the atmosphere for 48 hours is performed, Subsequently, carbonization heat treatment was performed among the vacuum by the processing condition held for 10 minutes at the temperature of 800 **, PVB was carbonized and the activated carbon boards for evaluation (70 mm long which are activated carbon and a complex of carbon black, the side of 50 mm, and 1 mm in thickness) were produced.

[0039]Next, after using the activated carbon boards for evaluation as an electrode and charging for 30 minutes on the voltage of 0.9V among an electrolysis solution, respectively, The electric capacity per electrode unit volume (F/cc) was calculated by the constant-current-discharge method of 30 mA/cm²

and 300 mA/cm², and the capacity factor of the electric capacity at the time of low current discharge of 30 mA/cm² to the electric capacity at the time of high-electric-current discharge of 300 mA/cm² was computed.

[0040]Evaluation of the mechanical strength of said activated carbon boards set distance between fulcrums to 30 mm using a specimen 1 mm in thickness, 4 mm in width, and 40 mm in length, made crosshead speed 0.5mm/min., and computed it from breaking load.

[0041]Next, as evaluation of a moldability, the crushing state and mold-release characteristic of the granulated body when said activated carbon boards were fabricated were observed and judged.

[0042]It impregnated with the organic solvent which changes from carbon compounds to an activated carbon substrate, and also the activated carbon sample which added and produced the binder was made into the comparative example.

[0043]

[Table 1]

| 試料 番号 | カーボン ブラック 重量部 | 静電容量(F/CC) | | 容量比 B/A ×100 (%) | 機械的 強 度 g/mm ² | 成形性 | 備 考 |
|----------|---------------------|-------------------|-------------------|---------------------------|---------------------------------|-----|----------|
| | | 低電流 放 電 (A) | 高電流 放 電 (B) | | | | |
| * 1 | — | 29.7 | 5.0 | 16.8 | 662 | 可 | |
| 2 | 0.5 | 35.5 | 17.6 | 49.6 | 631 | 良 | ケチエンブラック |
| 3 | 1.0 | 36.0 | 18.3 | 50.8 | 618 | 優 | " |
| 4 | 2.0 | 36.9 | 19.6 | 53.1 | 592 | " | " |
| 5 | 3.0 | 37.8 | 21.0 | 55.6 | 566 | " | " |
| 6 | 5.0 | 40.2 | 24.7 | 61.4 | 482 | 良 | " |
| 7 | 8.0 | 42.5 | 28.1 | 66.1 | 388 | " | " |
| 8 | 10.0 | 43.0 | 29.5 | 68.6 | 325 | " | " |
| * 9 | 15.0 | 46.1 | 36.3 | 78.7 | 96 | 不 良 | " |
| 10 | 0.5 | 30.5 | 12.3 | 40.3 | 647 | 良 | アセレンブラック |
| 11 | 1.0 | 31.3 | 12.8 | 40.9 | 634 | 優 | " |
| 12 | 2.0 | 31.9 | 13.5 | 42.3 | 608 | " | " |
| * 13 | — | 21.3 | 4.5 | 21.1 | 153 | 不 良 | 比較例 |

*印を付した試料番号は本発明の請求範囲外のものである。

[0044]The sample number 13 of a comparative example is 21.3 F/cc in electric capacity also low current discharge so that clearly from a table.

Are very low in 4.5 F/[cc and], and the high-electric-current discharge of a capacity factor is very as insufficient as 21.1%, In the sample number 9 in which what does not contain carbon black which is outside the generic claim of this invention has the comparable characteristic, and the content of carbon black exceeds ten weight sections for it. Although electric capacity and a capacity factor are satisfied, a moldability is very bad, a mechanical strength is inferior, and practicality is missing.

[0045]Each was satisfied with this invention of electric capacity and a capacity factor to them, and it was checked that a mechanical strength is also high and a moldability is also good.

[0046]Things cannot be overemphasized that this invention should just be what is not limited to said example and satisfies the main point of this invention.

[0047]